UV Photodissociation Of Furan Probed by Tunable Synchrotron Radiation

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INTRODUCTION

Unimolecular dissociation pathways of cyclic molecules play an important role in the combustion of organic matter.[1] It is believed that chemical pathways leading to the destruction and formation of cyclic molecules determine the fate of combustion by-products such as polycyclic aromatic hydrocarbons (PAHs) and in soot formation.[1,2] Unimolecular dissociation (or thermal decomposition) of molecules in combustion processes occurs as a result of the elevated temperatures, and dissociation proceeds mostly on the ground state potential energy surface (PES). Pyrolytic studies of cyclic compounds has yielded useful information on the thermal decomposition of many cyclic molecules.[3-7] These studies are, however, complicated by the presence of multiple secondary reactions and rigorous computer modeling must be done to determine the primary processes.[3] Photochemical studies in molecular beams, on the other hand, can provide unambiguous information on the primary processes following unimolecular dissociation.

In this abstract, we will present results for the ultraviolet photodissociation of furan obtained on the Chemical Dynamics Beamline at the Advanced Light Source. The unique combination of photofragment translational spectroscopy with intense, tunable undulator radiation available on the Beamline allows for detailed investigation of complex polyatomic dissociation dynamics, as has been shown for a number of systems[8].

Figure 1. A schematic representation of the photodissociation of furan and the observed primary dissociation pathways.

Ultraviolet excitation of polyatomic molecules is often rapidly followed by internal conversion to the ground state potential surface. When the corresponding dynamics are clearly distinct from those involving excited electronic states, one may study ground state dissociation dynamics under collision free conditions and at well-defined energies. Furthermore, excited state dissociation dynamics can also be studied to yield information about the nature of the excited state PES's.
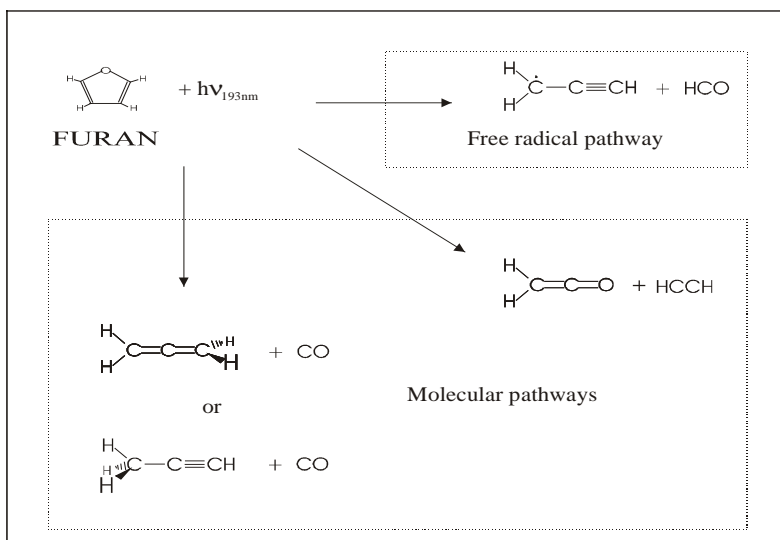
SUMMARY OF RESULTS

The radical channel

The strongest signal was found for the radical channel. Figure 2 shows the measured time-of-flight (TOF) spectra for HCO and C_3H_3 fragments. Although this channel was not observed in the pyrolytic studies of furan, it was proposed as a key reaction for producing free radicals. Our results clearly show the presence of this primary process. Furthermore, this channel appears to be the major one since the signal is the strongest.

In these measurements we utilized one of the advantages of tunable VUV radiation to photo-ionize the products. Photo-ion

Figure 2. TOF spectra for m/e 29 (HCO) and m/e 39 (C_3H_3) fragments

efficiency (PIE) spectra were measured for m/e 29 and 39 . From the PIE spectra, we have established the identity of m/e 39 as the propargyl radical. Figure 3 shows the PIE spectra for m/e 29 and m/e 39.

The angular distribution of the products of this channel was measured and was found to be anisotropic with a β parameter of -0.2. A negative β indicates that the transition dipole moment has a component perpendicular to the dissociation coordinate. Also, a nonzero β indicates that dissociation occurs on a rapid time scale relative to the rotational period.
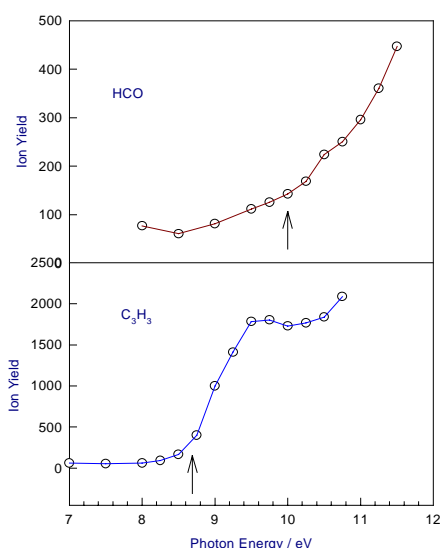
Figure 3. PIE spectra for m/e 29 and 39. These fragments have been identified as HCO and propargyl radical, respectively. The arrows indicate the known ionization onsets for these free radicals.

The molecular channels: CO + C$_3$H$_4$

For m/e 28, CO, the momentum-matched partner is m/e 40, C_3H_4. Both of these fragments show large contributions from the dominant radical channel shown above. Measured TOF spectra for these two masses at 20° and 50° are shown in Fig. 4. Figure 5 shows the PIE spectrum for m/e 40. The identity of m/e 40 product is more challenging to establish since the two likely isomers of C_3H_4 – propyne and allene – have similar ionization potentials, 10.36 eV and 9.69 eV, respectively. There appear to be two ionization onsets in the photoion yield
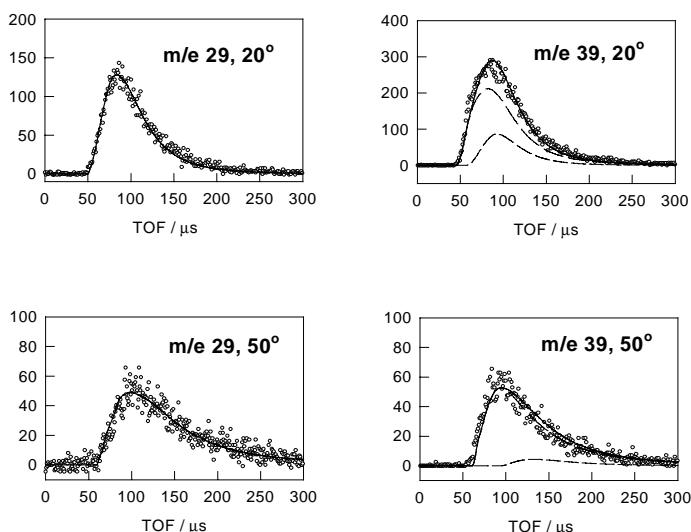
spectrum in Fig. 5, one at 8.75 eV and another at 10.25 eV. The ionization onset at 8.75 eV is identical to that shown above for m/e 39, the propargyl radical. The signal for m/e 39 is about 100 times larger than that for m/e 40, so that a small contribution resulting from mass leakage in the quadrupole from m/e 39 to the m/e 40 signal is responsible for the observation of two onsets. By scaling the m/e 39 contribution at the obvious break that appears in both spectra, we can subtract this contribution to obtain the PIE spectrum for the m/e 40 contribution alone, shown by the dashed line in Fig. 5.

Figure 4. TOF spectra for m/e 28 (CO) and 40 (C_3H_4) at laboratory angles of 20° and 50°.

The corrected signal for m/e 40 shows an onset of 9.5 eV. This is near the threshold for allene; however, as these are largely vibrationally excited products, we anticipate a significant red-shift in the ionization onset. As a result, it is most likely due to propyne, consistent with the findings of Liu, *et al*. whose calculations indicated that ground state unimolecular dissociation of furan to CO + propyne followed a path 23 kcal/mol lower in energy than the path leading to CO + allene.[10] The angular measurements for this fragment yielded an istropic distribution, thereby indicating that the process occurs on a *slow* time scale relative to the period of molecular rotation. The experimental evidence suggests that this reaction occurs on the ground state potential energy surface following internal conversion.
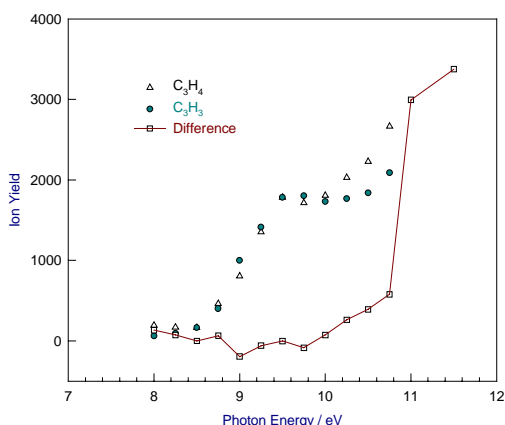

Figure 5. PIE spectra for m/e 40. A large contribution from m/e 39 was observed for this mass and after subtraction, a distinct ionization onset is realized. The m/e 40 fragment has been identified at propyne.
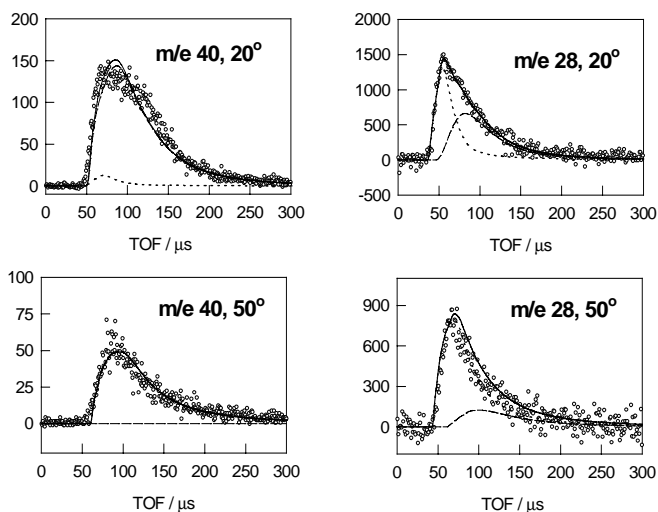
C_2H_2 + ketene

The TOF spectra for the momentum-matched fragments m/e 26 (acetylene, C_2H_2) and m/e 42 (ketene, H_2CCO) were recorded as for the two channels mentioned above. Due to lack of space, the data for this channel is not shown here. A potential energy barrier of 25 kcal/mol was found for this channel and is in reasonable agreement with the calculated value of 35 kcal/mol[10] and the experimentally derived value of 33 kcal/mol[7] for the ground state unimolecular dissociation of furan to acetylene and ketene. This channel is believed to occur on the ground state PES following internal conversion and a larger fraction of the available energy is released into the translational degrees of freedom of the products.

CONCLUSIONS
We have studied the dissociation dynamics of furan at 193 nm using photofragment translational spectroscopy with tunable VUV probe provided by intense synchrotron radiation. Three product channels are observed. Two of these result in closed shell molecular products and occur on the

ground electronic surface following internal conversion. The results for these channels are consistent with recent theoretical studies and shock-tube results. The third channel gives rise to radical products and is shown to occur as a direct process on an electronically excited potential energy surface.

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